

Optimization of Process Parameters in the Catalytic Degradation of Polypropylene to Liquid Fuel by Taguchi Method

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Abstract

In this study, Taguchi method was used to identify the factors and their interactions that may affect the thermo-catalytic degradation of waste polypropylene to liquid fuel in a batch reactor. The yield of liquid fuel in this process was greatly influenced by factors, such as temperature and catalyst concentration. By using orthogonal experimental design and analysis technique, the performance of this process can be analyzed with more objective conclusion through only a small number of simulation experiments. Analysis of variance (ANOVA) was carried out to identify the significant factors affecting the response and the best possible factor level combination was determined. Finally, a regression model for yield of liquid fuel from catalytic degradation of waste polypropylene has been developed, as a function of process parameters. It was found that yield of liquid fuel in this process was highly dependent on temperature followed by catalyst concentration.

Keywords

Taguchi Method; Thermo-catalytic Degradation; ANOVA; Waste Polypropylene; Liquid Fuel; Batch Reactor

Introduction

Polypropylene is widely used as industrial and household thermoplastics due to its diversified applications. Its contribution is 40% of the total global polyolefins demand during 2009 and is expected to increase in coming years. As the lives of plastic components are usually low, extensive use of these plastics would accumulate more wastes and create solid waste problem. Among the different recycling techniques, energy recovery is a more attractive option in which the waste plastics are thermally or catalytically degraded into gases and oils, which can be used as resources for fuels or chemicals. Catalytic

degradation of waste plastics is preferred to thermal pyrolysis due to narrow product distribution, high reaction rate and lower temperature of degradation. [Panda et al. (2010)].

A number of studies on the catalytic cracking of PP using different catalysts have been conducted by different investigators.

Audisio et al. have reported the catalytic degradation of polypropylene under vacuum in a semi batch reactor, using catalysts as Al_2O_3 , SiO_2 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, and Na-Y, H-Y and REY zeolites, at temperatures between 200°C and 600°C [Audisio et al. (1984)]. The thermal degradation of polypropylene powder by thermogravimetric analysis employs four different heating rates over different type of zeolite catalysts such as BEA, ZSM-5 and MOR with different surface areas, pore structures, acidities and Si/Al molar ratios [Durmus et al., (2005)]. The catalytic degradation of polypropylene has been investigated using solid acid catalysts, such as silica-alumina and zeolites (HZSM-5, natural zeolite, Mordenite etc.), in the range of 350°C to 450°C. The acidity and characteristic pore structure of this zeolite appear to be responsible for the good performance [Hwang et al. (1998)]. The catalytic degradation of polypropylene using silica-alumina in a semi batch reactor under a nitrogen flow has been investigated [Ishihara et al. (1989)]. The performance of several differently treated clinoptilolite zeolites (dealuminated clinoptilolite catalysts) in the degradation of polypropylene was investigated in a semi-batch reactor at 400°C [Kim et al. (2002)]. Lin et al. used a laboratory catalytic fluidised-bed reactor to obtain a range of volatile hydrocarbons by degradation of polypropylene in the temperature range from 290°C

to 430°C using different zeolitic and non zeolitic catalysts such as HZSM-5, HMOR and HUSY, MCM-41 and SAHA and found product streams varied markedly depending on catalysts type and structure [Lin et al. (2005)]. The thermogravimetric study of the thermal and catalytic decomposition (with MCM-41, ZSM-5 and an FCC as a catalyst) of polypropylene shows that the addition of MCM-41 produces a remarkable decrease of almost 110°C in the temperature of maximum decomposition rate [Marcilla et al. (2003)]. Negelein et al. have investigated the catalytic cracking of polypropylene by silica-alumina and H-ZSM-5 at temperatures between 350°C and 420°C and sulfated zirconia at temperatures below 300°C, also by means of thermogravimetry under helium flow [Negelein et al. (1998)].

Catalytic cracking of polypropylene has been carried out in a semi batch stirred reactor using spent equilibrium catalyst from FCC units, large pore zeolites as well as amorphous and ordered silica-alumina in order to study extensively the influence of pore size (micro and meso), crystallite size and the number and strength of the active acid sites [Salvador et al. (2000)]. Sakata et al. studied the catalytic cracking of polypropylene with silica-alumina catalyst at 380°C in a semi batch reactor without external gas flow [Sakata et al. (1996)].

Zhao et al. have studied the effects of different zeolites as H-Y, Na-Y, H-mordenite and Na-mordenite on the catalytic degradation of polypropylene by thermogravimetry under nitrogen flow [Zhao et al. (1996)]. Again they found that the degradation temperature of polypropylene strongly depended on the type of zeolite used, the amount added and one type of HY zeolite (320HOA) was shown to be a very effective catalyst [Zhao et al. (1996)].

The kinetics of the thermal and catalytic decomposition of Polypropylene using different contents of an acid catalyst such as MCM-41 has been studied using dynamic thermogravimetry at a heating rate of 10 K/min, under atmospheric pressure and inert atmosphere (N₂). The thermal and catalytic decomposition of PP shows that the addition of MCM-41 produces a remarkable decrease of almost 110°C at the temperature of maximum decomposition rate [Marcilla et al. (2003)].

From the above literature survey, it was observed that Kaolin has not been studied extensively in the thermal degradation of plastics wastes. Again kaolin, being a clay material, is thermally stable, which would support cracking reactions at high temperature. In

addition, the cost of the material is lower as compared to other catalysts used. So in the present work, studies have been carried out for the optimisation of catalytic degradation of polypropylene in batch reactor using kaolin as catalyst, with a view to optimize the yield of liquid fraction. The process parameters such as temperature and catalyst concentration have been identified which influence the decomposition of waste polypropylene in a batch process and Taguchi method was used to optimize the parameters for the production of liquid fuel from waste polypropylene.

Materials and Methods

In this experiment, waste polypropylene (disposable glass) was degraded using kaolin clay catalyst which affects the process. The waste polypropylene is identified by the DSC of the sample that gives the melting point of the waste sample to be 171°C, which ensures the samples to be polypropylene. Commercial grade kaolin clay procured from Chemtex Corporation, Kolkata, India, was used as catalyst in the pyrolysis reaction. The chemical composition of the kaolin sample was found to be SiO₂ 43.12%, Al₂O₃ 46.07%, Fe₂O₃ nil, MgO 0.027%, CaO 0.030%, ZnO 0.0064%, K₂O 0.01%, TiO₂ 0.74, LOI at 1000°C 9.9% [Panda et al. (2010)]. The pyrolysis setup used in this experiment is a batch reactor consisting of a reactor made of stainless steel tube. 20 g of waste polypropylene samples were loaded in each pyrolysis reaction. In the catalytic pyrolysis, a mixture of catalyst and the plastics samples in different catalyst to plastics proportion was subjected to pyrolysis at different temperatures ranging from 400-550°C in the batch reactor set up and heated at a rate of 20°C/min up to the desired temperature. The condensable liquid products were collected through the condenser and weighed. After pyrolysis, the solid residue left out inside the reactor was weighed. Then the weight of gaseous product was calculated from the material balance.

The statistical analysis has been done using MINITAB 14 software with Taguchi method in which reducing the variation is involved in a process through robust design of experiments. The overall objective of the method is to produce high quality product at low cost to the manufacturer. Therefore, poor quality in a process affects not only the manufacturer but also society. This is a method for designing experiments to investigate how different parameters affect the mean and variance of a process performance characteristic that defines how well the process functions. The experimental design proposed by Taguchi involves

using orthogonal arrays to organize the parameters affecting the process and the levels at which they should be varied; allowing for the collection of the necessary data to determine which factors most affect product quality with a minimum amount of experimentation, thus saving time and resources. Analysis of variance on the collected data from the Taguchi design of experiments can be used to select new parameter values to optimize the performance characteristic [Taguchi et al. (2005)].

Design of experiments in present work

Taguchi Approach to Parameter Design

In the present work, experimental work has been designed in a sequence of steps to insure that data is obtained in a way that its analysis will lead immediately to validating statistical inferences. This research methodology is termed as DESIGN OF EXPERIMENT (DOE) methodology. DOE using Taguchi approach attempts to extract maximum important information with minimum number of experiments [Lazic (2004)]. Taguchi techniques are experimental design optimization techniques which use standard Orthogonal Arrays (OA) to form a matrix of experiments. Using an OA to design the experiment helps the designer to study the influence of multiple controllable factors on the average of quality characteristics and the variations in a fast and economic way. OA's allow screening out few important main effects from the many less important ones. Also it allows us to estimate interaction effects if any and determine their significance [Taguchi et al. (2005)].

In the present reaction system, two operating parameters (Temperature and Plastics to catalyst ratio), each at three levels, are selected to evaluate yield of liquid fuel. The factors to be studied are mentioned in Table 1.

TABLE 1 FACTORS AND THEIR LEVELS IN THE EXPERIMENTAL DESIGN

| Level | Temperature [T] (°C) | Plastics to catalyst ratio [CR] |
|-------|----------------------|---------------------------------|
| 1 | 450 | 3 |
| 2 | 500 | 6 |
| 3 | 550 | 10 |

Based on Taguchi method, the experiments were carried out according to the L₁₆-OA. The reason for using L₁₆-OA is to evaluate the significance of interaction terms. Interaction means the influence of an operating variable on the effect of other operating variable [Mendenhall & Sincich (1989)].

Analysis of data

After conducting the experiment, the results were converted into mean values. The final L₁₆-OA display response values and their corresponding mean-values for yield of liquid fuel. Main effects plot for the main effect terms viz. factors T and CR are shown in Figure 1. From the main effect plots, it has been observed that yield of liquid fuel increases with increment in temperature from 450°C to 500°C and decreases with further increment in temperature from 500°C to 550°C due to the formation of more non condensable gaseous/volatile fractions by rigorous cracking at higher temperature. Yield of liquid fuel increases with increment in plastic to catalyst ratio owing to the increase in the acid centers, which is mainly responsible for cracking process.

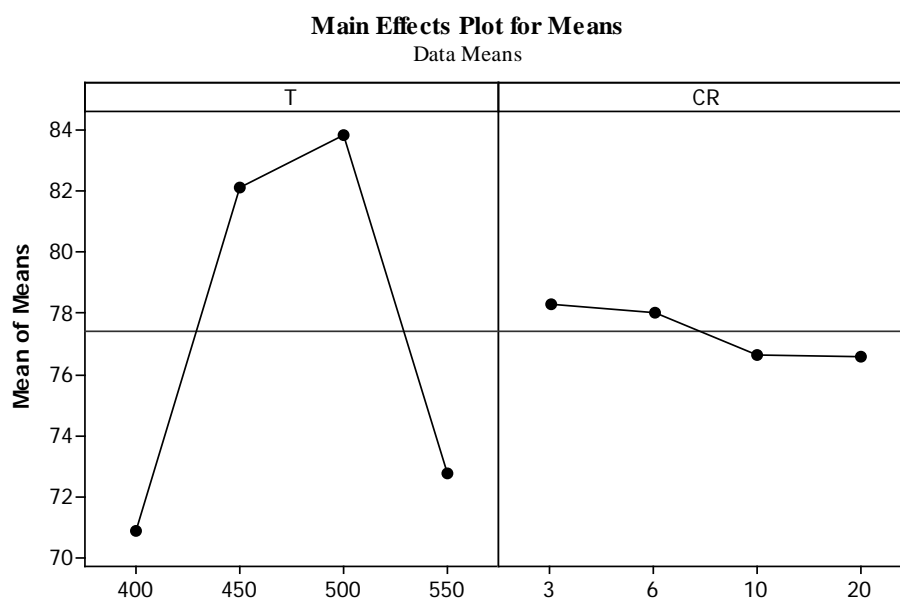


FIGURE 1 MAIN EFFECT PLOTS

Result Evaluation

There are two different methodologies in carrying out the complete OA analysis. A common approach is to analyze the average result of repetitive runs, or a singlerun, through ANOVA analysis [Lazic (2004)]. Since in the present work there is only one replication, further analysis of OA is done through ANOVA. Once the data for a designed experiment have been collected, the sample information is used to make inferences about the population means associated with the various treatments. The method used to compare the treatment means is known as analysis of variance, or ANOVA [Mendenhall & Sincich (1989)].

An ANOVA Table breaks down the effect of each factor and the experimental error. In addition, it will also break down all of the possible interactions of the factors. In the present work, ANOVA Table for yield of liquid fuel from waste polypropylene has been shown in Table 2 using MINITAB 14 software. In this process, it is seen that the significant factors are temperature (T) and plastic to catalyst ratio (CR), written in the decreasing order of significance.

TABLE 2 ANALYSIS OF VARIANCE FOR MEANS (ANOVA).

| Source | DF | SS | MS | P |
|----------------|----|---------|---------|-------|
| T | 3 | 510.013 | 170.004 | 0.000 |
| CR | 3 | 9.542 | 3.181 | 0.115 |
| Residual error | 9 | 10.907 | 1.212 | |
| Total | 15 | 530.462 | | |

It is seen that the interaction terms has completely vanished. The final ANOVA Table for percentage contribution (exact value in percent) of each of the significant factors in affecting the response value, which is calculated on the basis of ANOVA Table, is shown in Table 3. The significant main effect terms and interaction terms in the ANOVA are computed using the F-ratio as a test statistic [Mendenhall & Sincich (1989)].

TABLE 3 FINAL ANOVA TABLE

| Source | DF | SS | MS | F-Ratio | Percentage contribution [SS/SS(Total)*100] |
|--------------|----|---------|---------|---------|---|
| T | 3 | 510.013 | 170.004 | 99.767 | 96.145 |
| Total | 15 | 530.462 | | | |
| Pooled error | 12 | 20.449 | 1.704 | | |

In the process of catalytic decomposition of waste polypropylene in a batch reactor, the ranks indicate that temperature has the greatest influence followed by plastic to catalyst ratio, which can be observed in Table 4. The optimum condition in this case where in the percentage degradation of waste polypropylene is

maximum is at temperature: 500°C, catalyst type in terms of acidity: 0.21 mmol/g and plastic to catalyst ratio: 3.

TABLE 4 RESPONSE TABLE FOR MEAN (LARGER IS BETTER)

| Level | T | CR |
|-------|-------|-------|
| 1 | 70.88 | 78.32 |
| 2 | 82.13 | 78.01 |
| 3 | 83.83 | 76.66 |
| 4 | 72.78 | 76.61 |
| Delta | 12.95 | 1.71 |
| Rank | 1 | 2 |

Mathematical Modeling

A general regression for the complete model was performed using MINITAB 14 software. Regression in MINITAB 14 uses the ordinary least squares method which derives the equation by minimizing the sum of the squared residuals. In the present study, there are three operational factors each at three levels. The complete model for the degradation of pollutants is shown below. The number of terms in the model depends on the degree of freedom of the main effect terms and the corresponding interactions.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_1^2 + \beta_3 x_2 + \beta_4 x_2^2 + \beta_5 x_1 x_2 + \beta_6 x_1 x_2^2 + \beta_7 x_1^2 x_2 + \beta_8 x_1^2 x_2^2 \quad (1)$$

y = yield percentage of liquid fuel; β = model coefficients; x_1 , x_2 = dimensionless coded factors for temperature, plastic to catalyst ratio respectively.

TABLE 5 ESTIMATED MODEL COEFFICIENTS FOR MEANS

| Term | Coefficient | SE coefficient | T | P |
|----------|-------------|----------------|---------|-------|
| Constant | 77.4019 | 0.2752 | 281.245 | 0.000 |
| x_1 | -6.5269 | 0.4767 | -13.692 | 0.000 |
| x_1^2 | 4.7231 | 0.4767 | 9.908 | 0.000 |
| x_1^3 | 6.4231 | 0.4767 | 13.475 | 0.000 |

A simpler reduced model of lower order which provides sufficient information for the prediction of y was found using the F-test statistic [Mendenhall & Sincich (1989)]. If $F > F_\alpha$, $\alpha = 0.05$, then the reduced model doesn't provide sufficient information and is rejected. A t-test of individual parameters in the regression model was further performed. The t value for each parameter is enlisted in the MINITAB 14 software program [Table 5]. To test the null hypothesis $H_0: \beta_i = 0$ against the alternative hypothesis $\beta_i \neq 0$, a two tailed t-test was performed and H_0 was rejected if $t > t_{\alpha/2}$ or $t < -t_{\alpha/2}$ ($\alpha = 0.05$). The level of confidence is 95 % i.e. p-value should be less than 0.05. If p-value is less than 0.05, it shows doubt on null hypothesis, which says all sample means equal and effect of that factor on the result is statistically significant [Mendenhall & Sincich (1989)]. The final prediction equation obtained

from MINITAB 14 software for the yield of liquid fuel by the catalytic decomposition of waste polypropylene is as per equation (1).

$$y = 77.4019 - 6.5269x_1 + 4.7231x_1^2 + 6.4231x_1^3 \quad (2)$$

The coefficients of model for means are shown in Table 5.

$S = 1.101$ $R^2 = 97.9\%$ $R^2(\text{adj}) = 96.6\%$, the parameter R^2 describes the amount of variation observed in yield is explained by the input factors. $R^2 = 97.9\%$ indicates that the model is able to predict the response with high accuracy. Adjusted R^2 is a modified R^2 that has been adjusted for the number of terms in the model. If unnecessary terms are included in the model, R^2 can be artificially high, but adjusted R^2 ($=96.6\%$) may get smaller. The standard deviation of errors in the modeling, $S = 1.101$ indicates that model can explain the variation in yield of liquid fuel to the extent of 97.9%, which makes the model adequate to represent the process.

The residual plot for means of this process is shown in Figure 2. This layout is useful to determine whether the model meets the assumptions of the analysis. The residuals are the deviations of the observed data values from the predicted value \hat{y} and estimate the error terms (e_i) in the model [Mendenhall & Sincich (1989)]. The e_i is assumed to be random and normally distributed with mean equal to zero and constant

standard deviation. If the error terms follow a normal distribution, they will fall on a straight line on the normal probability plot. Because they are estimates of the error terms, the residuals should exhibit similar properties. If the assumptions are valid, plots of the residuals versus run sequence, predicted values, and other independent variables should be random and structure less. If structure remains in the residuals, residual plots may suggest modifications to the model that will remove the structure. Investigation of residuals has been used to evaluate the model adequacy. Residuals are found to be scattered and without any definite pattern which prove the adequacy of the model.

The residual plots in the Figure 2 and the interpretation of each residual plot for the present experiment is given below:

- Normal probability plot indicates that the data are normally distributed and the variables influence the response. Outliers don't exist in the data
- Residuals versus fitted values indicate that the variance is constant and a non-linear relationship exists.
- Histogram proves the data are not skewed and no outliers exist.
- Residuals versus order of the data indicate that there are systematic effects on the data due to time or data collection order.

Residual Plots for Means

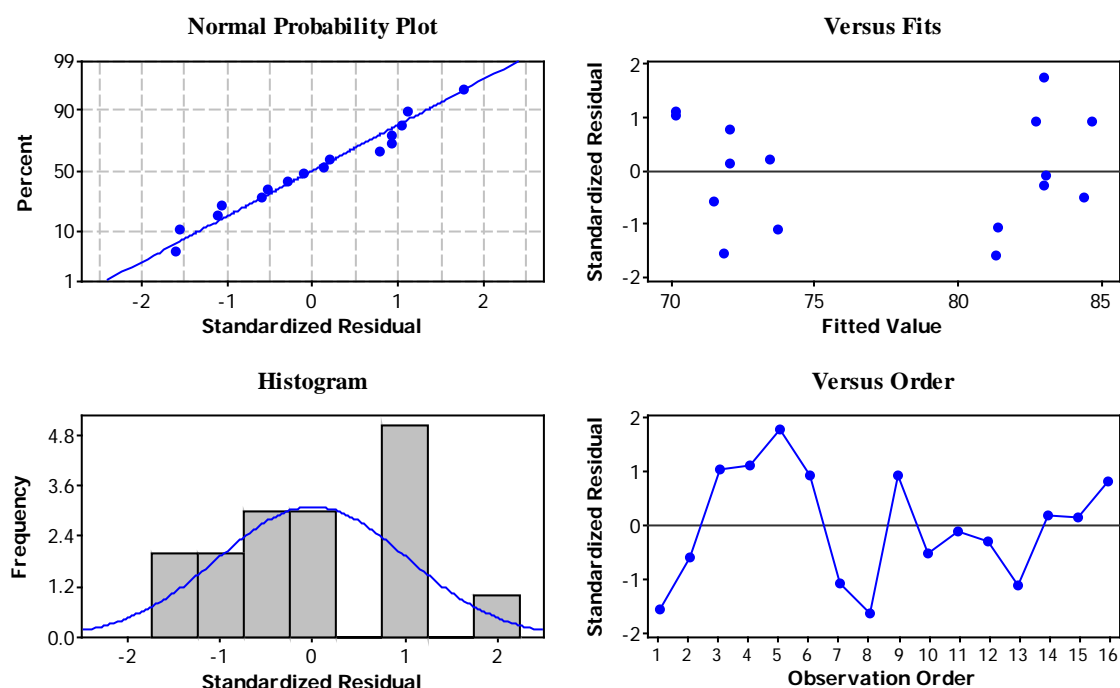


FIGURE 2 DIFFERENT RESIDUAL PLOTS FOR TESTING THE ADEQUACY OF THE PROPOSED MODEL.

Conclusion

With these experiments, we upgraded our existing knowledge about the influence of the different process parameters on the yield of liquid fuel in a batch process and thus contributing to improving the process's reliability. This study has shown the application of Taguchi method on the performance evaluation of a chemical process for the production of liquid fuel from waste plastics in a batch reactor. The level of importance of the process's parameters was determined by using ANOVA. Moreover, regression modeling has helped us generate an equation to describe the statistical relationship between the process's parameters and the response variable (yield of liquid fuel) and to predict new observations. The simulation experiment was successful in terms of achieving the objective of experiment, which was to quantify the main effects as well as interactions of potentially influential factors on the degradation of pollutants.

Appendix: Nomenclature

DF: Degree of freedom

SS: Sum of squares

MS: Mean of squares

S/N: Signal to noise ratio

s: Standard deviation

R-sq: Regression squared

R-sq(adj): Adjusted regression

REFERENCES

- Audisio, G., Silvani, A., Beltrame, P.L., and Carniti, P., (1984). Catalytic thermal degradation of polymers : Degradation of polypropylene. *J Anal Appl Pyrol.* 7, 83-90.
- Clements, R.B., 1991. *Handbook of Statistical Methods in Manufacturing*. Prentice Hall, New Jersey
- Durmus, A., NaciKoc, S., SeldaPozan, G., and Kasgoz, A. (2005). Thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites. *Appl. Catal., B.* 61, 316–322.
- Hwang, E.Y., Choi, J.K., Kim, D.H., Park, D.W., and Woo, H.C., (1998). Catalytic degradation of polypropylene i. Screening of catalysts. *Korean J Chem Eng.*, 15(4), 434-438.
- Ishihara, Y., Nanbu, H., Iwata, C., Ikemura, T., and Takesue, T., (1989). The Catalytic Degradation Reaction of Polypropylene with Silica–Alumina. *Bull. Chem. Soc. Jpn.*, 62, 2981-1988.
- Kim, J.R., Kim, Y.A., Yoon, J.H., Park, D.W. and Woo, H.C. (2002). Catalytic degradation of polypropylene: effect of dealumination of clinoptilolite catalyst. *Polym.Degrad. Stab.*, 75, 287–294.
- Lazic, Z.R., 2004. *Design of Experiments in Chemical Engineering*. WILEYVCH, Weinheim.
- Lin, Y.H., and Yen, H.Y., (2005). Fluidised bed pyrolysis of polypropylene over cracking catalysts for producing hydrocarbons. *Polym Degrad Stab.*, 89, 101-108.
- Marcilla, A., Go'mez, A., Reyes-Labarta, J.A., and Giner, A., (2003). Catalytic pyrolysis of polypropylene using MCM-41: kinetic model. *Polym Degrad Stab.*, 80, 233–240.
- Mendenhall, W., Sincich, T., 1989. *Statistics for the engineering and computer sciences*, second ed. Maxwell Macmillan, Singapore.
- Negelein, D.L., Lin, R., and White, R.L., (1998). Effects of catalyst acidity and structure on polymer cracking mechanisms.. *J Appl. Pol. Sc.*, 67, 341-349.
- Panda, A.K., Singh, R.K., and Mishra, D.K. (2010). Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective. *Renew Sustain Energ Rev.*, 14(1), 233-248.
- Panda, A.K., et al., 2010. Effect of Sulphuric acid treatment on the physicochemical characteristics of Kaolin clay, *Colloids Surf., A*, 363 (1-3), 98-104.
- Sakata, Y., Uddin, M.A., Koizumi, K. and Murata, K., (1996). Catalytic Degradation of Polypropylene into Liquid Hydrocarbons Using Silica-Alumina Catalyst. *Chem letters.* 8, 245-251.
- Taguchi, G., Chowdhury, S., Wu, Y., 2005. *TAGUCHI'S Quality Engineering Handbook*. John Wiley & Sons, New Jersey.
- Zhao, W., Hasegawa, S., Fujita, J., Yoshii, F., Sasaki, T. and Makuuchi, K., (1996). Effect of irradiation on pyrolysis of polypropylene in the presence of zeolite. *Polym. Degrad. Stab.*, 53, 199-206.
- Zhao, W., Hasegawa, S., Fujita, J., Yshii, F., Sasaki, T., Makuuchi, K., et al., 1996. Effects of zeolites on the pyrolysis Polypropylene, *Polymer Degradation and Stability* 53, 129-135.



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